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要約

(57)【要約】

【課題】充放電サイクルによる性能劣化が少なく、長期の作動信頼性に優れた電気二重層コンデンサを提供する。

【解決手段】有機電解液の電気二重層コンデンサにおいて、活性炭を主体とする電極と集電体との間に、付加重合型のイミド基含有化合物をバインダ成分として含む導電性接着層を介在させる。

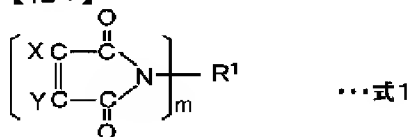
請求の範囲

【特許請求の範囲】

【請求項1】炭素材料を主体とする電極を導電性接着層を介して集電体と接合してなる電極体と、前記電極体との界面に電気二重層を形成する有機電解液と、を有する電気二重層コンデンサにおいて、前記導電性接着層が、バインダ成分として付加重合型のイミド基含有化合物を含有する懸濁液の硬化物からなることを特徴とする電気二重層コンデンサ。

【請求項2】前記イミド基含有化合物は、式1で表されるポリマレイミド、式1で表されるポリマレイミドとジアミンとの反応物、及び式1で表されるポリマレイミドと式2で表されるジシアネート化合物との反応物からなる群から選ばれる1種以上である請求項1記載の電気二重層コンデンサ。

【化1】



(ただし、X、Yはそれぞれ独立に水素原子又は1価の有機基であり、 R^1 は炭素数2以上のm価の有機基であって、mは2～10の整数である。)

【化2】

$\text{N} \equiv \text{C} \text{---} \text{O} \text{---} \text{Ph} \text{---} \text{R}^2 \text{---} \text{Ph} \text{---} \text{O} \text{---} \text{C} \equiv \text{N} \cdots \text{式2}$ (ただし、 ---Ph--- はフェニレン基であり、 R^2 は単結合、S、O、 CH_2 、 SO_2 又は $\text{C}(\text{CH}_3)_2$ を表す。)

【請求項3】前記電極は、バインダとして含フッ素樹脂が含まれる請求項1又は2記載の電気二重層コンデンサ。

【請求項4】有機電解液の溶質が、第4級アンモニウム塩又は第4級ホスホニウム塩である請求項1、2又は3記載の電気二重層コンデンサ。

【請求項5】炭素材料を主体とする電極を導電性接着層を介して集電体と接合してなる電極体と、前記電極体との界面に電気二重層を形成する有機電解液と、を有する電気二重層コンデンサの製造方法において、前記電極をシート状に成形した後、バインダ成分として付加重合型のイミド基含有化合物を含有する導電性接着剤を介して集電体に接合し、 200°C 以上で加熱乾燥することを特徴とする電気二重層コンデンサの製造方法。

詳細な説明

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は電気二重層コンデンサ、特に作動信頼性に優れた電気二重層コンデンサに関する。

【0002】

【従来の技術】電気二重層コンデンサは、電極と電解液との界面に形成される電気二重層に電荷を蓄積することを原理としており、電気二重層コンデンサの容量密度を向上させるため、電極には高比表面積の活性炭、カーボンブラック等の炭素材料、金属又は導電性金属酸化物の微粒子等が用いられる。充電及び放電を効率よく行うため、電極は集電体と呼ばれる金属や黒鉛等の電子伝導性の抵抗の小さい層や箔に接合されている。集電体には通常電気化学的に耐食性の高いアルミウム等のバルブ金属、SUS304、SUS316L等のステンレス鋼等が使用されている。

【0003】電気二重層コンデンサには、電解液として有機電解液を用いたものと水系電解液を用いたものがあるが、作動電圧が高く、充電状態のエネルギー密度を大きくできる点で有機電解液を用いた電気二重層コンデンサが注目されている。有機電解液を用いる場合、電気二重層コンデンサの内部に水分が存在すると、水分が電気分解して性能の劣化を招くため、電極は充分に脱水する必要がある、通常、減圧下で加熱する乾燥処理が施されている。

【0004】電極には主に活性炭が使用されるが、活性炭は通常粉末状であるため、例えばポリテトラフルオロエチレン(以下、PTFEという)等の含フッ素樹脂を含むバインダと混合してシート状電極に成形し、集電体と電氣的に接続させた電極体として用いることが知られている。このとき、電極と集電体を密着させ、か

つ電気的な接触抵抗が小さくなるように、導電性接着層を介して接合したものも多くある。しかし、含フッ素樹脂は接着が難しい性質を有しており、接合強度を高くすることが難しい。

【0005】導電性接着層は電気化学的な耐食性を必要とされるので、電子伝導性を与えるフィラーとしてカーボンブラックや黒鉛等の非金属系材料を含むことが好ましい。さらに接合強度を確保するため、導電性接着層には種々のバインダ成分が使用される。該バインダ成分としては、セルロース、ポリビニルアルコール等の樹脂(特開昭59-3915、特開昭62-200715)、水ガラス等の無機系バインダ成分(特開平2-82608)や、ポリイミド系樹脂(特開平9-270370)が知られている。

【0006】しかし、セルロース、ポリビニルアルコール等の樹脂系バインダ成分を含む導電性接着剤を用いた場合、有機電解液に対する耐性が不十分なため、電極と集電体が剥離しやすい。また、耐熱温度が120℃前後であるため高温で乾燥処理ができず、電極と集電体を接合した後には活性炭に吸着している残存水分を充分には除去しがたく、その残存水分が電気分解して有機溶媒系電気二重層コンデンサの性能が劣化する等の問題がある。また、水ガラス等の無機系バインダでは、耐熱性は高いものの電極と金属集電体との接合強度が不十分であり、アルカリ成分の溶出や残留水分によって電気二重層コンデンサの性能劣化が起こる問題がある。

【0007】

【発明が解決しようとする課題】本発明は上記従来技術における問題点を解決し、電極中の水分をきわめて少なくすることができ、電極と集電体との接合強度が強く、充放電サイクルにより性能劣化の起きにくい電気二重層コンデンサ及びその製造方法を提供することを目的とする。

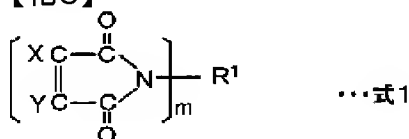
【0008】

【課題を解決するための手段】本発明は、炭素材料を主体とする電極を導電性接着層を介して集電体と接合してなる電極体と、前記電極体との界面に電気二重層を形成する有機電解液と、を有する電気二重層コンデンサにおいて、前記導電性接着層が、バインダ成分として付加重合型のイミド基含有化合物を含有する懸濁液の硬化物からなることを特徴とする電気二重層コンデンサ及びその製造方法を提供する。

【0009】本発明における付加重合型のイミド基含有化合物としては、式1で表されるポリマレイミド、式1で表されるポリマレイミドとジアミンとの反応物、式1で表されるポリマレイミドと式2で表されるジシアネート化合物との反応物等が好ましい。これらの化合物は、接着特性に優れており、熱硬化させることにより付加重合し、耐熱性と機械的強度のバランス及び耐蝕性に優れた樹脂となる。

【0010】

【化3】



【0011】(ただし、X、Yはそれぞれ独立に水素原子又は1価の有機基であり、 R^1 は炭素数2以上のm価の有機基であって、mは2~10の整数である。)

【0012】

【化4】

$\text{N} \equiv \text{C} \text{---} \text{O} \text{---} \text{Ph} \text{---} \text{R}^2 \text{---} \text{Ph} \text{---} \text{O} \text{---} \text{C} \equiv \text{N} \cdots \text{式2}$ 【0013】(ただし、 ---Ph--- はフェニレン基であり、 R^2 は単結合、S、O、 CH_2 、 SO_2 又は $\text{C}(\text{CH}_3)_2$ を表す。)

【0014】式1で表されるポリマレイミドにおいて、 $\text{---R}^1 \text{---}$ で表される有機基の具体例を挙げると、 ---Ph--- 、 $\text{---Ph---CH}_2 \text{---Ph---}$ 、 ---Ph---O---Ph--- 、 $\text{---Ph---SO}_2 \text{---Ph---}$ 等が挙げられる。ただし、本明細書において、 ---Ph--- はフェニレン基を示す。

【0015】また、X、Yはそれぞれ独立に水素原子又は1価の有機基であるが、その分子量は小さい方が架橋反応が進行しやすい点で好ましく、特にX、Yともに水素原子であることが好ましい。本発明ではX又はYがハロゲンからなるポリマレイミドは使用できない。例えばX又はYが塩素原子であると、塩化水素が発生して電極を腐食することがある。また、mは $2 \leq m \leq 10$ の整数である。

【0016】式1で表されるポリマレイミドの具体例を挙げると、以下の化合物が挙げられる。N、N'ーエチレンビスマレイミド、N、N'ーヘキサメチレンビスマレイミド、N、N'ー(1,3-フェニレン)ビスマレイミド、

N, N' - [1, 3 - (2 - メチルフェニレン)]ビスマレイミド、N, N' - (1, 4 - フェニレン)ビスマレイミド、ビス(4 - マレイミドフェニル)メタン、ビス(3 - メチル - 4 - マレイミドフェニル)メタン、ビス(4 - マレイミドフェニル)エーテル、ビス(4 - マレイミドフェニル)スルホン、ビス(4 - マレイミドフェニル)スルフィド、ビス(4 - マレイミドフェニル)ケトン、ビス(4 - マレイミドシクロヘキシル)メタン。

【0017】1, 4 - ビス(4 - マレイミドフェニル)シクロヘキサン、1, 4 - ビス(マレイミドメチル)シクロヘキサン、1, 4 - ビス(マレイミドメチル)ベンゼン、1, 3 - ビス(4 - マレイミドフェノキシ)ベンゼン、1, 3 - ビス(3 - マレイミドフェノキシ)ベンゼン。

【0018】ビス[4 - (3 - マレイミドフェノキシ)フェニル]メタン、ビス[4 - (4 - マレイミドフェノキシ)フェニル]メタン、1, 1 - ビス[4 - (3 - マレイミドフェノキシ)フェニル]エタン、1, 1 - ビス[4 - (4 - マレイミドフェノキシ)フェニル]エタン、1, 2 - ビス[4 - (3 - マレイミドフェノキシ)フェニル]エタン、1, 2 - ビス[4 - (4 - マレイミドフェノキシ)フェニル]エタン、2, 2 - ビス[4 - (3 - マレイミドフェノキシ)フェニル]プロパン、2, 2 - ビス[4 - (4 - マレイミドフェノキシ)フェニル]プロパン、2, 2 - ビス[4 - (3 - マレイミドフェノキシ)フェニル]ブタン、2, 2 - ビス[4 - (4 - マレイミドフェノキシ)フェニル]ブタン、2, 2 - ビス[4 - (3 - マレイミドフェノキシ)フェニル] - 1, 1, 1, 3, 3, 3 - ヘキサフルオロプロパン、2, 2 - ビス[4 - (4 - マレイミドフェノキシ)フェニル] - 1, 1, 1, 3, 3, 3 - ヘキサフルオロプロパン。

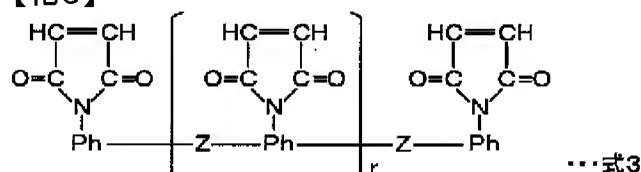
【0019】4, 4' - ビス(3 - マレイミドフェノキシ)ビフェニル、4, 4' - ビス(4 - マレイミドフェノキシ)ビフェニル、ビス[4 - (3 - マレイミドフェノキシ)フェニル]ケトン、ビス[4 - (4 - マレイミドフェノキシ)フェニル]ケトン、ビス[4 - (3 - マレイミドフェノキシ)フェニル]スルフィド、ビス[4 - (4 - マレイミドフェノキシ)フェニル]スルフィド、ビス[4 - (3 - マレイミドフェノキシ)フェニル]スルホキシド、ビス[4 - (4 - マレイミドフェノキシ)フェニル]スルホキシド、ビス[4 - (3 - マレイミドフェノキシ)フェニル]スルホン、ビス[4 - (4 - マレイミドフェノキシ)フェニル]スルホン。

【0020】ビス[4 - (3 - マレイミドフェノキシ)フェニル]エーテル、ビス[4 - (4 - マレイミドフェノキシ)フェニル]エーテル、1, 4 - ビス[4 - (4 - マレイミドフェノキシ) - α , α - ジメチルベンジル]ベンゼン、1, 3 - ビス[4 - (4 - マレイミドフェノキシ) - α , α - ジメチルベンジル]ベンゼン、1, 4 - ビス[4 - (3 - マレイミドフェノキシ) - α , α - ジメチルベンジル]ベンゼン、1, 3 - ビス[4 - (3 - マレイミドフェノキシ) - α , α - ジメチルベンジル]ベンゼン、1, 4 - ビス[4 - (4 - マレイミドフェノキシ) - 3, 5 - ジメチル - α , α - ジメチルベンジル]ベンゼン、1, 3 - ビス[4 - (4 - マレイミドフェノキシ) - 3, 5 - ジメチル - α , α - ジメチルベンジル]ベンゼン、1, 4 - ビス[4 - (3 - マレイミドフェノキシ) - 3, 5 - ジメチル - α , α - ジメチルベンジル]ベンゼン、1, 3 - ビス[4 - (3 - マレイミドフェノキシ) - 3, 5 - ジメチル - α , α - ジメチルベンジル]。

【0021】さらに、式3で表される化合物も使用できる。このポリマレイミド化合物は、アニリンとホルムアルデヒド又は α , α' - ジクロロ - p - キシレンとの反応生成物であるポリアミンと無水マレイン酸とを酸性触媒下に縮合、脱水反応をさせて得られるポリマレイミド化合物である。上記に例示したポリマレイミドは、単独でも2種以上を混合して使用してもよい。

【0022】

【化5】



【0023】(ただし、Zはメチレン基又はp - キシリレン基であり、 $0 < r \leq 8$ 。)

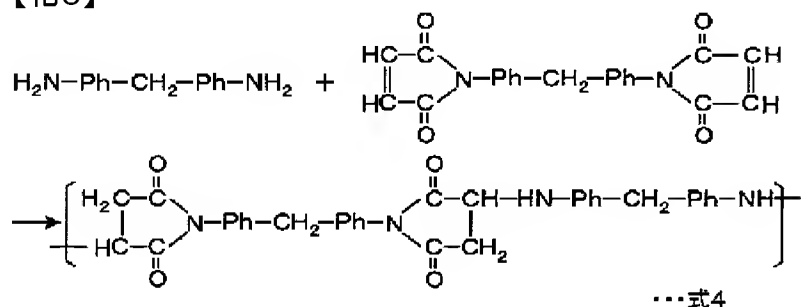
【0024】本発明において式1で表されるポリマレイミドと反応させるジアミンは、ポリマレイミドと反応可能なジアミンであれば特に限定されない。具体的な例を挙げると、下記の化合物が挙げられる。

【0025】ジエチレントリアミン、トリエチレンテトラミン、テトラエチレンペンタミン、ヘキサメチレンジアミン、N - アミノエチルピペラジン、1, 4 - ビス(アミノプロピル)ピペラジン、トリメチルヘキサメチレンジアミン、メタフェニレンジアミン、パラフェニレンジアミン、4, 4' - ジアミノジフェニルメタン、4, 4' - ジアミノジフェニルプロパン、4, 4' - ジアミノジフェニルエタン、4, 4' - ジアミノジフェニルスルフォン、3, 3' - ジアミノジフェニルスルフォン、パラ - ビス(4 - アミノフェノキシ)ベンゼン、メタ - ビス(4 - アミノフェノキシ)ベンゼン。

ン、4, 4'-ジアミノジフェニルエーテル、4, 4'-ジアミノジフェニルスルフィド、1, 5-ジアミノナフタレン、3, 4'-ジアミノベンズアニリド、3, 4'-ジアミノジフェニルエーテル、3, 3'-ジメトキシベンジジン、メタキシリレンジアミン、パラキシリレンジアミン。これらのジアミンは単独でも2種以上混合して用いてもよい。
【0026】本発明において、式1で表されるポリマレイミドとジアミンとの反応物とは、例えば下記の反応により得られる化合物が挙げられる。

【0027】

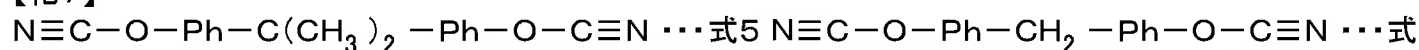
【化6】



【0028】本発明において式1で表されるポリマレイミドと反応させるジシアネートは式2で表されるが、その具体例としては例えば下記の化合物が挙げられる。

【0029】

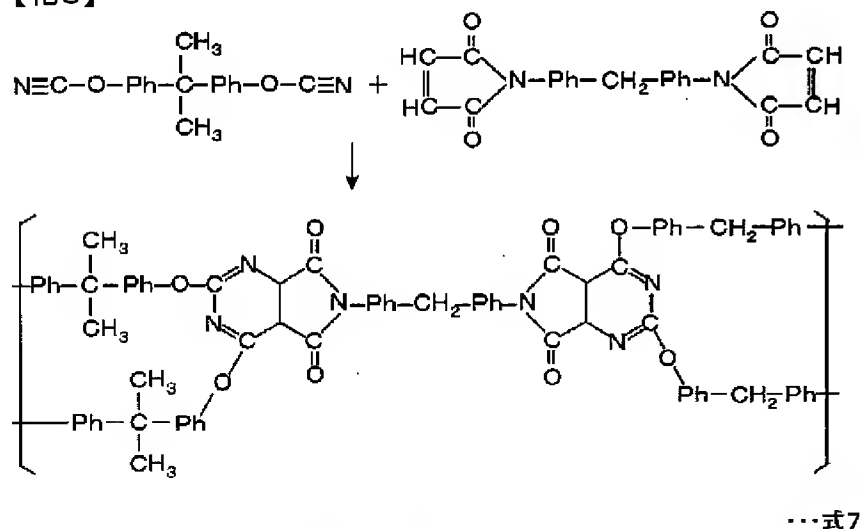
【化7】



【0030】また、本発明における式1で表されるポリマレイミドと式2で表されるジシアネート化合物との反応物としては、例えば下記の反応により得られる化合物が挙げられる。

【0031】

【化8】



【0032】本発明における電極と集電体とを接合するための導電性接着剤は、バインダ成分として上記の付加重合型のイミド基含有化合物を含有する懸濁液であり、導電性を付与するために導電性粉末が含まれる。導電性粉末としては金属系、非金属系のものがあるが、金属系の粉末は局部電池を作る可能性があるため、非金属系導電性粉末を用いることが好ましい。導電性粉末は電気的な耐食性を必要とされるので、カーボンブラックや黒鉛等の炭素系材料の使用が特に好ましい。

【0033】また導電性粉末は、バインダとなる樹脂との濡れ性、分散性を改善するために、該粉末に対し1重量%程度の脂肪酸、各種シランカップリング剤等の表面処理剤を混合して表面処理を行ってもよい。その他にレベリング剤、分散剤等の添加剤を加えてもよい。

【0034】本発明において、導電性接着層に含まれる付加重合型のイミド基含有化合物の割合は、導電性粉末と付加重合型のイミド基含有化合物との含量に対し、10～70重量%であることが好ましい。10重

量%未満では接着層の強度が低下し良好な接着性が得られず、70重量%を超えると導電性が急激に低下するため好ましくない。特に20～60重量%が好ましい。

【0035】本発明の電気二重層コンデンサでは、導電性接着層のバインダ成分である、付加重合型のイミド基含有化合物の硬化物の耐熱性が高いため、電極と集電体を接合した後も高温下での加熱又は減圧下の加熱処理によって活性炭中にある水分を高度に乾燥除去できる。また、上記硬化物は有機電解液に対する耐性があり、含フッ素樹脂をバインダとする電極シートの金属等の集電体への接着強度もきわめて優れる。このため、大電流密度で充放電サイクルを繰り返しても長期間にわたって電圧を印加しても作動性能が安定しており、電極の内部抵抗の増加も小さくできる。

【0036】導電性接着剤を用いて集電体と電極を接合させるには、付加重合型のイミド基含有化合物は粉末又はワニスとして入手して溶剤に溶解し、これに導電性フィラーとしてカーボンブラックや黒鉛微粒子を高度に分散させた懸濁液を接着剤として使用する。この接着剤は集電体の表面に塗工し、次いでこの表面に別途作製した電極シートをのせて圧着し、好ましくは200℃以上の高温下、さらには減圧下で加熱乾燥することにより集電体と電極を強固に接合できる。

【0037】上記溶剤としては、付加重合型のイミド基含有化合物を溶解でき、加熱乾燥させる工程で蒸発するものであれば特に限定されず、各種溶剤を使用できる。具体的には、N-メチル-2-ピロリドン、ジメチルホルムアミド、アセトン、メチルエチルケトン、テトラヒドロフラン、キシレン、クロロホルム、トルエン、ジメチルスルホキシド、シクロヘキサン、アセトニトリル、ジオキサン、ジメチルエーテル等が挙げられ、これらの溶剤は単独でも2種以上混合して用いてもよい。

【0038】本発明の電気二重層コンデンサの電極の炭素材料は、比表面積が700～2500m²/g、特に1000～2000m²/gであると容量が大きく強度も高くできるので好ましい。炭素材料としては活性炭、カーボンブラック、ポリアセン等が挙げられるが、特に活性炭粉末を使用することが好ましく、導電材として高導電性カーボンブラックを加えて使用するとさらに好ましい。この場合、導電材は電極中に5～20重量%含まれることが好ましい。

【0039】また、通常、正極、負極ともに上記電極を用いて電気二重層コンデンサを構成するが、正極又は負極の一方のみを上記電極とし、もう一方の電極に充放電可能な非分極性電極材料、すなわち二次電池用活物質材料を主成分として使用してもよい。

【0040】本発明における電極にはバインダとして含フッ素樹脂が含まれることが好ましい。特にポリテトラフルオロエチレンは耐熱性、耐薬品性を有し、繊維化させることにより少量でも電極に強度を付与し、電極の導電性を阻害しにくいので好ましい。電極の強度と導電性のバランスの観点から、バインダは電極中に5～20重量%含まれることが好ましい。

【0041】上記の電極を電氣的に接続する集電体は、導電性に優れ、かつ電気化学的に耐久性のある材料であればよく、アルミニウムやチタンやタンタル等のバルブ金属、ステンレス鋼、金や白金等の貴金属、黒鉛やグラッシーカーボンやカーボンブラックを含む導電性ゴム等の炭素系材料等が好ましく使用できる。特に軽量で導電性に優れ電気化学的に安定していることからアルミニウムが好ましい。

【0042】電極はシート状に成形した後、導電性接着剤を介して集電体に接合されることが好ましく、電極の作製方法としては、例えば活性炭粉末とカーボンブラックと含フッ素樹脂と液状潤滑材との混合物を混練した後圧延してシート状に成形する。得られたシート状電極はあらかじめ集電体に導電性接着剤を塗工した面の上にのせて圧着し、好ましくは200℃以上の高温下、さらに好ましくは減圧下で加熱乾燥することにより導電性接着剤が硬化して強固に集電体と電極を接合できる。電極体の生産性向上のためには250～400℃で減圧乾燥することがさらに好ましい。

【0043】また、電極は、含フッ素樹脂を溶媒に溶解した溶液に炭素材料を分散させてスラリーとなし、該スラリーを集電体に塗工して形成してもよい。この場合もスラリーは、あらかじめ集電体に導電性接着剤を塗工した面の上に塗工し、200℃以上の高温下、特に減圧下で加熱乾燥することが好ましい。

【0044】本発明の電気二重層コンデンサに使用される有機電解液は特に限定されず、公知の有機溶媒にイオン解離性の塩類を含む有機電解液を使用できる。なかでもR¹R²R³R⁴N⁺、R¹R²R³R⁴P⁺ (R¹、R²、R³、R⁴、はそれぞれ独立に炭素数1～6のアルキル基)等の第4級オニウムカチオンと、BF₄⁻、PF₆⁻、ClO₄⁻、CF₃SO₃⁻等のアニオンとからなる塩を有機溶媒に溶解させた有機電解液を使用するのが好ましい。

【0045】上記有機溶媒としては、プロピレンカーボネート、ブチレンカーボネート、ジエチルカーボネート等のカーボネート類、 γ -ブチラクトン等のラクトン類、スルホラン又はこれらの混合溶媒が好ましく使用できる。

【0046】た有機電解液を使用するのが好ましい。

【0047】

【実施例】以下、本発明を実施例(例1～5)及び比較例(例6)によってさらに説明するが、本発明はこれらに限定されない。

【0048】水蒸気賦活法で得られたやしがら活性炭粉末(平均粒径 $10\mu\text{m}$ 、比表面積 $1800\text{m}^2/\text{g}$)80重量%、PTFE10重量%及びカーボンブラック10重量%からなる混合物にエタノールを加えて混練し、混練物をシート状に成形し、さらに厚さ0.3mmにロール圧延した。このシートから40mm角の電極シートを切り取り、エッチング処理を施したアルミニウム箔(厚さ0.1mm)からなる集電体の表面に以下に示す導電性接着剤を塗工し、この表面に圧着し、減圧下で3時間加熱して乾燥処理をした。乾燥後、アルゴンガスで充満したグローブボックスに移し、有機電解液として1モル/リットルのテトラエチルアンモニウムテトラフルオロボレートを含むプロピレンカーボネート溶液を電極に充分含浸させ、ポリプロピレン繊維の不織布からなるセパレータ紙を2枚の電極間に挟んで対向させ、電気二重層コンデンサを組み立てた。

【0049】得られた電気二重層コンデンサの初期の放電容量及び内部抵抗を測定した後、 40°C の恒温槽中で0～2.8Vの間で1Aの定電流による充放電を3000サイクル繰り返し、3000サイクル後の放電容量及び内部抵抗を測定した。充放電サイクル前後の性能変化を比較することにより、電気二重層コンデンサの長期的な作動信頼性を加速的に評価した。結果を表1に示す。

【0050】[導電性接着剤(1)]ビスマレイミドとビスフェノールAジシアネートが主成分であるビスマレイミド・トリアジン樹脂(三菱瓦斯化学社製、商品名:BT2170)を20重量%含むアセトン溶液25gに黒鉛微粒子5gを分散させ、これを導電性接着剤(1)とした。

【0051】[導電性接着剤(2)]BT2170のかわりにビス(4-マレイミドフェニル)メタン(三井東圧化学社製、商品名:BMI-S)を4.5gと4,4'-ジアミノジフェニルメタン(三井東圧化学社製、商品名:MDA-220)を0.5g、アセトンのかわりにジメチルホルムアミドを用いた以外は導電性接着剤(1)と同様にして導電性接着剤(2)を調製した。

【0052】[導電性接着剤(3)]黒鉛微粒子の代わりに導電性カーボンブラック粉末を用いた以外は導電性接着剤(1)と同様にして導電性接着剤(3)を調製した。

【0053】[導電性接着剤(4)]アセトンのかわりにメチルエチルケトンを用い、BT2170の濃度を40重量%とした以外は導電性接着剤(1)と同様にして導電性接着剤(4)を調製した。

【0054】[導電性接着剤(5)]BT2170のかわりに無水マレイン酸と4,4'-ジアミノジフェニルメタンが主成分であるポリアミノビスマレイミド樹脂(ロール・プーラン社製、商品名:ケルイミド601)を用いた以外は導電性接着剤(3)と同様にして導電性接着剤(5)を調製した。

【0055】[導電性接着剤(6)]BT2170のかわりにポリビニルアルコール(日本合成化学社製、商品名:ゴーセノール)を用いた以外は導電性接着剤(1)と同様にして導電性接着剤(6)を調製した。

【0056】なお、電極シートと集電体とを接合するために減圧乾燥する温度は、使用する接着剤のバインダーの耐熱温度を考慮し、表1のとおりとした。

【0057】

【表1】

	導電性 接着剤	減圧乾燥 の温度	初期物性		サイクル試験後	
			容量／F	抵抗／Ω	容量／F	抵抗／Ω
例1	(1)	300℃	15.4	0.50	14.6	0.50
例2	(2)	300℃	15.3	0.51	14.6	0.50
例3	(3)	300℃	15.5	0.51	14.7	0.50
例4	(4)	300℃	15.0	0.53	14.5	0.51
例5	(5)	300℃	15.2	0.52	15.6	0.51
例6	(6)	120℃	14.4	0.66	8.4	1.30

【0058】

【発明の効果】本発明によれば、電極シートと集電体との間に介在する導電性接着剤の耐熱温度が高く、かつ接着力が強固であるため、充放電サイクルによる性能劣化が少ない電気二重層コンデンサを提供できる。

PATENT ABSTRACTS OF JAPAN

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(54) ELECTRIC DOUBLE LAYER CAPACITOR AND METHOD OF PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To strengthen junction strength of an electrode to a collector by decreasing water in the electrode by forming a conductive adhesion layer of a hardened suspension containing an addition-polymerized imino group-containing compound as a binder component.

SOLUTION: An addition-polymerized imido group-containing compound preferably includes polymaleimide expressed by formula I (where each of X and Y is independently hydrogen atom or monovalent organic group, R1 is m-valent organic group with two carbon atoms or more and m is integer from 1 to 10), a reactant of polymaleimido expressed by the formula I and diamine, and a reactant of polymaleimide

expressed by the formula I and a dicyanate compound expressed by formula II (where -Ph- is phenylene group, R2 is single bond S, O, CH2, SO2 a C(CH3)2). These compounds have excellent adhesion characteristics and becomes resins excellent in balance of heat resistance and mechanical strength, and corrosion resistance by addition-polymerization by thermosetting them.

CLAIMS

[Claim(s)]

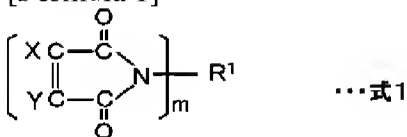
[Claim 1]An electric double layer capacitor consisting of a hardened material of suspension in which said conductive glue line contains an addition condensation type imido group content compound as a binder component in an electric double layer capacitor characterized by comprising the following.

An electrode body which joins an electrode which makes a carbon material a subject to a charge collector via a conductive glue line.

Organic electrolysis liquid which forms an electric double layer in an interface with said electrode body.

[Claim 2]A reactant of polymaleimide as which said imido group content compound is expressed in the formula 1, polymaleimide expressed with the formula 1, and diamine, And the electric double layer capacitor according to claim 1 which is one or more sorts chosen from a group which consists of a reactant with a JISHIANETO compound expressed with polymaleimide expressed with the formula 1, and the formula 2.

[Formula 1]



(However, X and Y are a hydrogen atom or a univalent organic group independently, respectively, R¹ is an organic group of with a carbon numbers of two or more m value, and m is an integer of 2-10.)

[Formula 2]

N**C-O-Ph-R²-Ph-O-C**N ... Formula 2 (however, -Ph- is a phenylene group and R² expresses a single bond, S, O, CH₂, SO₂, or C(CH₃)₂.)

[Claim 3]The electric double layer capacitor according to claim 1 or 2 with which fluorine-containing resin is contained as a binder as for said electrode.

[Claim 4]The electric double layer capacitor according to claim 1, 2, or 3 whose solute of organic electrolysis liquid is quarternary ammonium salt or the 4th class phosphonium salt.

[Claim 5]In a manufacturing method of an electric double layer capacitor characterized by comprising the following. A manufacturing method of an electric double layer capacitor joining to a charge collector via electroconductive glue which contains an addition condensation type imido group content compound as a binder component, and carrying out stoving above 200 ** after fabricating said electrode to a sheet shaped.

An electrode body which joins an electrode which makes a carbon material a subject to a charge collector via a conductive glue line.

Organic electrolysis liquid which forms an electric double layer in an interface with said electrode body.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to an electric double layer capacitor, especially the electric double layer capacitor excellent in working reliability.

[0002]

[Description of the Prior Art] The electric double layer capacitor makes it the principle to accumulate an electric charge in the electric double layer formed in the interface of an electrode and an electrolysis solution.

In order to raise the capacity density of an electric double layer capacitor, the particles of carbon materials, such as activated carbon of high specific surface area and carbon black, metal, or conductive metallic oxide, etc. are used for an electrode.

In order to perform charge and discharge efficiently, the electrode is joined to the small layer and foil of resistance of electron conductivity of metal, black lead, etc. which are called a charge collector. Stainless steel, such as valve metals, such as corrosion-resistant high ARUMIUMU, SUS304, and SUS316L, etc. are usually electrochemically used for the charge collector.

[0003] Although there are what used organic electrolysis liquid as an electrolysis solution, and a thing using a drainage system electrolysis solution in an electric double layer capacitor, operating potential is high and the electric double layer capacitor using organic electrolysis liquid attracts attention at the point which can enlarge the energy density of a charging state. In order for moisture to electrolyze and to cause degradation of performance if moisture exists in the inside of an electric double layer capacitor when using organic electrolysis liquid, it is necessary to fully dry an electrode and the drying process heated under decompression is usually performed.

[0004] Although activated carbon is mainly used for an electrode, since activated carbon is usually powdered, it mixes with the binder which contains fluorine-containing resin, such as polytetrafluoroethylene (henceforth PTFE), for example, and fabricates to a sheet like electrode, and using as an electrode body electrically connected to the charge collector is known. At this time, there are also many things joined via the conductive glue line so that an electrode and a charge collector may be stuck and electric contact resistance may become small. However, it is difficult for fluorine-containing resin for adhesion to have difficult character and to make bonding strength high.

[0005] Since electrochemical corrosion resistance is needed for a conductive glue line, it is preferred that nonmetal system materials, such as carbon black and black lead, are included as a filler which gives electron conductivity. In order to secure bonding strength furthermore, various binder components are used for a conductive glue line. As this binder component, inorganic system binder components (JP,2-82608,A), such as resin (JP,59-3915,A, JP,62-200715,A), such as cellulose and polyvinyl alcohol, and water glass, and polyimide system resin (JP,9-270370,A) are known.

[0006] However, since the tolerance over organic electrolysis liquid is insufficient when the electroconductive glue containing resin system binder components, such as cellulose and polyvinyl alcohol, is used, an electrode and a charge collector exfoliate easily. Since heat-resistant temperature is around 120 **, after a drying process is impossible at an elevated temperature and joining a charge collector to an electrode, it is fully hard to remove the residual moisture which is sticking to activated carbon, and the residual moisture electrolyzes and there is a problem of the performance of an organic solvent system electric double layer capacitor deteriorating. Inorganic system binders of heat resistance, such as water glass, are [the bonding strength of the electrode of a high thing

and a metal charge collector] insufficient, and there is a problem from which the performance degradation of an electric double layer capacitor arises with elution and residual water of an alkali component.

[0007]

[Problem(s) to be Solved by the Invention] This invention can solve the problem in the above-mentioned conventional technology, the moisture in an electrode can be lessened extremely, and the bonding strength of an electrode and a charge collector is strong, and aims at providing an electric double layer capacitor to which performance degradation cannot get up easily due to a charging and discharging cycle, and a manufacturing method for the same.

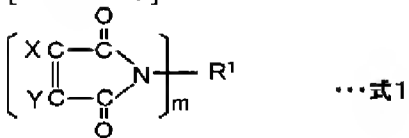
[0008]

[Means for Solving the Problem] In an electric double layer capacitor which has organic electrolysis liquid which forms an electric double layer in an interface of an electrode body by which this invention joins an electrode which makes a carbon material a subject to a charge collector via a conductive glue line, and said electrode body, Said conductive glue line provides an electric double layer capacitor consisting of a hardened material of suspension which contains an addition condensation type imido group content compound as a binder component, and a manufacturing method for the same.

[0009] As an addition condensation type imido group content compound in this invention, a reactant of polymaleimide expressed with the formula 1, polymaleimide expressed with the formula 1, and diamine, a reactant with a JISHIANETO compound expressed with polymaleimide expressed with the formula 1 and the formula 2, etc. are preferred. These compounds are excellent in the adhesion characteristic, and by making it heat-harden, addition condensation of them is carried out and they serve as resin excellent in balance of heat resistance and a mechanical strength, and corrosion resistance.

[0010]

[Formula 3]



[0011] (However, X and Y are a hydrogen atom or a univalent organic group independently, respectively, R^1 is an organic group of with a carbon numbers of two or more m value, and m is an integer of 2-10.)

[0012]

[Formula 4]

$\text{N}^{**}\text{C-O-Ph-R}^2\text{-Ph-O-C}^{**}\text{N}$... Formula 2 [0013] (However, -Ph- is a phenylene group and R^2 expresses a single bond, S, O, CH_2 , SO_2 , or $\text{C}(\text{CH}_3)_2$.)

[0014] In the polymaleimide expressed with the formula 1, if the example of an organic group expressed with $\text{-R}^1\text{-}$ is given, -Ph- , $\text{-Ph-CH}_2\text{-Ph-}$, -Ph-O-Ph- , $\text{-Ph-SO}_2\text{-Ph-}$, etc. will be mentioned. However, in this specification, -Ph- shows a phenylene group.

[0015] Although X and Y are a hydrogen atom or a univalent organic group independently, respectively, the smaller one of the molecular weight is preferred at the point that crosslinking reaction advances easily, and it is preferred that X and Y are especially hydrogen atoms. In this invention, X or Y cannot use the polymaleimide which consists of halogen. For example, when X or Y is a chlorine atom, hydrogen chloride

may occur and an electrode may be corroded. m is an integer of $2 \leq m \leq 10$.

[0016]The following compounds will be mentioned if an example of polymaleimide expressed with the formula 1 is given. N,N'-ethylene bismaleimide, N,N'-hexamethylene bismaleimide, N,N'-(1,3-phenylene) bismaleimide, N,N'-[1,3-(2-methylphenylene)] bismaleimide, N,N'-(1,4-phenylene) bismaleimide, bis(4-maleimide phenyl)methane, Bis(3-methyl-4-maleimide phenyl)methane, bis(4-maleimide phenyl)ether, A bis(4-maleimide phenyl)sulfone, a bis(4-maleimide phenyl)sulfide, bis(4-maleimide phenyl)ketone, bis(4-maleimide cyclohexyl)methane.

[0017]1,4-bis(4-maleimide phenyl)cyclohexane, 1,4-bis(maleimide methyl)cyclohexane, 1,4-bis(maleimide methyl)benzene, 1,3-bis(4-maleimide phenoxy)benzene, 1,3-bis(3-maleimide phenoxy)benzene.

[0018]Bis[4-(3-maleimide phenoxy) phenyl] methane, bis[4-(4-maleimide phenoxy) phenyl] methane, 1,1-bis[4-(3-maleimide phenoxy) phenyl] ethane, 1,1-bis[4-(4-maleimide phenoxy) phenyl] ethane, 1,2-bis[4-(3-maleimide phenoxy) phenyl] ethane, 1,2-bis[4-(4-maleimide phenoxy) phenyl] ethane, 2,2-bis[4-(3-maleimide phenoxy) phenyl] propane, 2,2-bis[4-(4-maleimide phenoxy) phenyl] propane, 2,2-bis[4-(3-maleimide phenoxy) phenyl] butane, 2,2-bis[4-(4-maleimide phenoxy) phenyl] butane, 2,2-screw [4-(3-maleimide phenoxy) phenyl]-1,1,1,3,3,3-hexafluoropropane, 2,2-screw [4-(4-maleimide phenoxy) phenyl]-1,1,1,3,3,3-hexafluoropropane.

[0019]4,4'-bis(3-maleimide phenoxy)biphenyl, 4,4'-bis(4-maleimide phenoxy)biphenyl, Bis[4-(3-maleimide phenoxy) phenyl] ketone, bis[4-(4-maleimide phenoxy) phenyl] ketone, A bis[4-(3-maleimide phenoxy) phenyl] sulfide, a bis[4-(4-maleimide phenoxy) phenyl] sulfide, A bis[4-(3-maleimide phenoxy) phenyl] sulfoxide, a bis[4-(4-maleimide phenoxy) phenyl] sulfoxide, a bis[4-(3-maleimide phenoxy) phenyl] sulfone, a bis[4-(4-maleimide phenoxy) phenyl] sulfone.

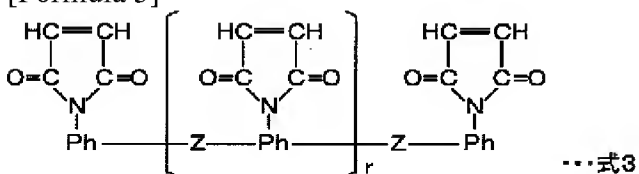
[0020]Bis[4-(3-maleimide phenoxy) phenyl] ether, bis[4-(4-maleimide phenoxy) phenyl] ether, 1,4-bis[4-(4-maleimide phenoxy)-alpha and alpha-dimethylbenzyl] benzene, 1,3-bis[4-(4-maleimide phenoxy)-alpha and alpha-dimethylbenzyl] benzene, 1,4-bis[4-(3-maleimide phenoxy)-alpha and alpha-dimethylbenzyl] benzene, 1,3-bis[4-(3-maleimide phenoxy)-alpha and alpha-dimethylbenzyl] benzene, 1,4-bis[4-(4-maleimide phenoxy)-3,5-dimethyl- alpha and alpha-dimethylbenzyl] benzene, 1,3-bis[4-(4-maleimide phenoxy)-3,5-dimethyl- alpha and alpha-dimethylbenzyl] benzene, 1,4-bis[4-(3-maleimide phenoxy)-3,5-dimethyl- alpha and alpha-dimethylbenzyl] benzene, a 1,3-screw [4-(3-maleimide phenoxy)-3,5-dimethyl- alpha and alpha-dimethylbenzyl].

[0021]A compound expressed with the formula 3 can also be used. This polymaleimide compound is a polymaleimide compound produced by making carry out condensation and dehydration under an acid catalyst in polyamine and a maleic anhydride which are resultants with aniline, formaldehyde or alpha, and alpha'-dichloro-p-xylene.

Polymaleimide illustrated above may be independent, or two or more sorts may be mixed and used for it.

[0022]

[Formula 5]



[0023](However Z being a methylene group or p-xylylene group $0 < r \leq 8$.)

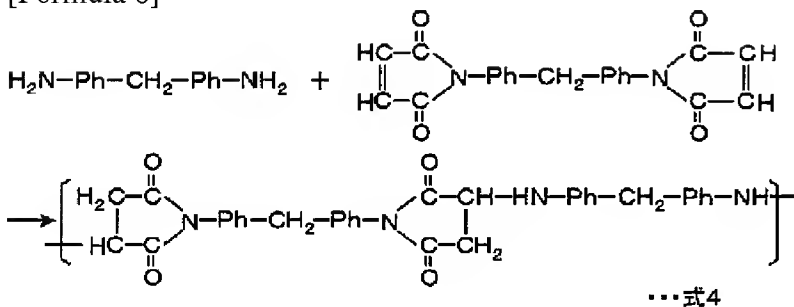
[0024]The diamine made to react to the polymaleimide expressed with the formula 1 in this invention will not be limited especially if it is polymaleimide and diamine in which a reaction is possible. The following compound will be mentioned if a concrete example is given.

[0025]Diethylenetriamine, triethylenetetramine, tetraethylenepentamine, Hexamethylenediamine, N-aminoethyl piperazine, a 1,4-bis(aminopropyl)piperazine, Trimethyl hexamethylenediamine, a meta-phenylenediamine, a p phenylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylpropane, 4,4'-diaminodiphenylethane, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone, Para -**** (4-aminophenoxy) benzene, Metha- bis(4-aminophenoxy)benzene, 4,4'-diaminodiphenyl ether, A 4,4'-diamino diphenyl sulfide, 1,5-diaminonaphthalene, a 3,4'-diaminobenzanilide, 3,4'-diaminodiphenyl ether, 3,3'-dimethoxybenzidine, meta-xylylene diamine, PARAKI silylenediamine. These diamine may be independent, or two or more sorts may be mixed and it may be used.

[0026]In this invention, a compound obtained by the reaction of the following [reactant / of polymaleimide and diamine which are expressed with the formula 1] for example, is mentioned.

[0027]

[Formula 6]



[0028]Although JISHIANETO made to react to the polymaleimide expressed with the formula 1 in this invention is expressed with the formula 2, the following compound is mentioned as the example.

[0029]

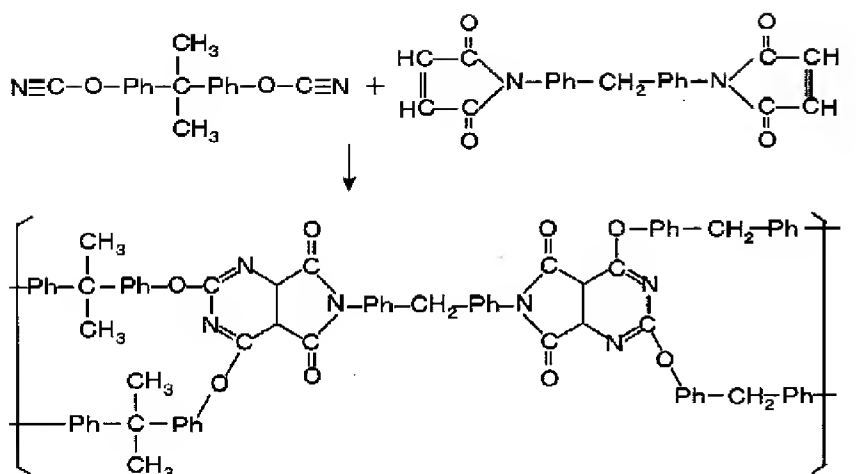
[Formula 7]

$\text{N}^{**}\text{C}-\text{O}-\text{Ph}-\text{C}(\text{CH}_3)_2-\text{Ph}-\text{O}-\text{C}^{**}\text{N} \dots$ Formula 5 $\text{N}^{**}\text{C}-\text{O}-\text{Ph}-\text{CH}_2-\text{Ph}-\text{O}-\text{C}^{**}\text{N} \dots$

Formula 6 [0030]The compound obtained, for example by the following reaction as a reactant with the JISHIANETO compound expressed with the polymaleimide expressed with the formula 1 in this invention and the formula 2 is mentioned.

[0031]

[Formula 8]



...式7

[0032]The electroconductive glue for joining the electrode and charge collector in this invention is suspension which contains an above-mentioned addition condensation type imido group content compound as a binder component, and conductive powder is contained in order to give conductivity. Although there is a thing of a metal system and a nonmetallic system as conductive powder, since the powder of a metal system may make a local cell, it is preferred to use nonmetal system conductive powder. Since electric corrosion resistance is needed for conductive powder, especially use of carbon system materials, such as carbon black and black lead, is preferred.

[0033]In order to improve wettability with resin used as a binder, and dispersibility, conductive powder may mix finishing agents, such as about 1% of the weight of fatty acid, and various silane coupling agents, to this powder, and may perform a surface treatment. In addition, additive agents, such as a leveling agent and a dispersing agent, may be added.

[0034]As for the rate of the addition condensation type imido group content compound contained in a conductive glue line, in this invention, it is preferred that it is 10 to 70 % of the weight to the total amount of conductive powder and an addition condensation type imido group content compound. At less than 10 % of the weight, since the intensity of a glue line falls, and conductivity will fall rapidly if a good adhesive property is not acquired but it exceeds 70 % of the weight, it is not desirable. 20 to 60 % of the weight is especially preferred.

[0035]In an electric double layer capacitor of this invention, since the heat resistance of a hardened material of an addition condensation type imido group content compound which is a binder component of a conductive glue line is high, also after joining a charge collector to an electrode, the dry removal of the moisture in activated carbon can be highly carried out by heating under an elevated temperature, or heat-treatment under decompression. The above-mentioned hardened material has the tolerance over organic electrolysis liquid, and adhesive strength to charge collectors, such as metal etc. of an electrode sheet which uses fluorine-containing resin as a binder, is also extremely excellent. For this reason, even if it repeats a charging and discharging cycle with large current density and impresses voltage over a long period of time, the operation performance is stable, and an increase in internal resistance of an electrode can also be

made small.

[0036]In order to join an electrode to a charge collector using electroconductive glue, an addition condensation type imido group content compound comes to hand as powder or a varnish, dissolves in a solvent, and uses as adhesives suspension which made this distribute carbon black and graphite particles highly as a conductive filler. Coating of these adhesives is carried out on the surface of a charge collector, they carry and stick by pressure an electrode sheet subsequently to this surface produced separately, and can join an electrode to a charge collector firmly by carrying out stoving under decompression further under a not less than 200 °C elevated temperature preferably.

[0037]As the above-mentioned solvent, an addition condensation type imido group content compound can be dissolved, especially if it evaporates at a process which carries out stoving, it will not be limited, but various solvents can be used. Specifically N-methyl-2-pyrrolidone, dimethylformamide, Acetone, methyl ethyl ketone, a tetrahydrofuran, xylene, chloroform, toluene, dimethyl sulfoxide, cyclohexane, acetonitrile, dioxane, wood ether, etc. may be mentioned, these solvents may be independent, or two or more sorts may be mixed and they may be used.

TECHNICAL FIELD

[Field of the Invention]This invention relates to an electric double layer capacitor, especially the electric double layer capacitor excellent in working reliability.

PRIOR ART

[Description of the Prior Art]The electric double layer capacitor makes it the principle to accumulate an electric charge in the electric double layer formed in the interface of an electrode and an electrolysis solution.

In order to raise the capacity density of an electric double layer capacitor, the particles of carbon materials, such as activated carbon of high specific surface area and carbon black, metal, or conductive metallic oxide, etc. are used for an electrode.

In order to perform charge and discharge efficiently, the electrode is joined to the small layer and foil of resistance of electron conductivity of metal, black lead, etc. which are called a charge collector. Stainless steel, such as valve metals, such as corrosion-resistant high ALUMINIUM, SUS304, and SUS316L, etc. are usually electrochemically used for the charge collector.

[0003]Although there are what used organic electrolysis liquid as an electrolysis solution, and a thing using a drainage system electrolysis solution in an electric double layer capacitor, operating potential is high and the electric double layer capacitor using organic electrolysis liquid attracts attention at the point which can enlarge the energy density of a charging state. In order for moisture to electrolyze and to cause degradation of performance if moisture exists in the inside of an electric double layer capacitor when using organic electrolysis liquid, it is necessary to fully dry an electrode and the drying process heated under decompression is usually performed.

[0004]Although activated carbon is mainly used for an electrode, since activated carbon is usually powdered, it mixes with the binder which contains fluorine-containing resin, such as polytetrafluoroethylene (henceforth PTFE), for example, and fabricates to a sheet

like electrode, and using as an electrode body electrically connected to the charge collector is known. At this time, there are also many things joined via the conductive glue line so that an electrode and a charge collector may be stuck and electric contact resistance may become small. However, it is difficult for fluorine-containing resin for adhesion to have difficult character and to make bonding strength high.

[0005] Since electrochemical corrosion resistance is needed for a conductive glue line, it is preferred that nonmetal system materials, such as carbon black and black lead, are included as a filler which gives electron conductivity. In order to secure bonding strength furthermore, various binder components are used for a conductive glue line. As this binder component, inorganic system binder components (JP,2-82608,A), such as resin (JP,59-3915,A, JP,62-200715,A), such as cellulose and polyvinyl alcohol, and water glass, and polyimide system resin (JP,9-270370,A) are known.

[0006] However, since the tolerance over organic electrolysis liquid is insufficient when the electroconductive glue containing resin system binder components, such as cellulose and polyvinyl alcohol, is used, an electrode and a charge collector exfoliate easily. Since heat-resistant temperature is around 120 **, after a drying process is impossible at an elevated temperature and joining a charge collector to an electrode, it is fully hard to remove the residual moisture which is sticking to activated carbon, and the residual moisture electrolyzes and there is a problem of the performance of an organic solvent system electric double layer capacitor deteriorating. Inorganic system binders of heat resistance, such as water glass, are [the bonding strength of the electrode of a high thing and a metal charge collector] insufficient, and there is a problem from which the performance degradation of an electric double layer capacitor arises with elution and residual water of an alkali component.

EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, highly [the heat-resistant temperature of the electroconductive glue which intervenes between an electrode sheet and a charge collector], since adhesive strength is firm, an electric double layer capacitor with little performance degradation by a charging and discharging cycle can be provided.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention can solve the problem in the above-mentioned conventional technology, the moisture in an electrode can be lessened extremely, and the bonding strength of an electrode and a charge collector is strong, and aims at providing an electric double layer capacitor to which performance degradation cannot get up easily due to a charging and discharging cycle, and a manufacturing method for the same.

MEANS

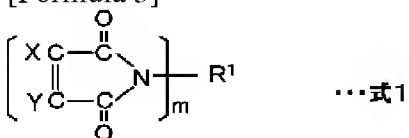
[Means for Solving the Problem] In an electric double layer capacitor which has organic electrolysis liquid which forms an electric double layer in an interface of an electrode body by which this invention joins an electrode which makes a carbon material a subject

to a charge collector via a conductive glue line, and said electrode body, Said conductive glue line provides an electric double layer capacitor consisting of a hardened material of suspension which contains an addition condensation type imido group content compound as a binder component, and a manufacturing method for the same.

[0009]As an addition condensation type imido group content compound in this invention, a reactant of polymaleimide expressed with the formula 1, polymaleimide expressed with the formula 1, and diamine, a reactant with a JISHIANETO compound expressed with polymaleimide expressed with the formula 1 and the formula 2, etc. are preferred. These compounds are excellent in the adhesion characteristic, and by making it heat-harden, addition condensation of them is carried out and they serve as resin excellent in balance of heat resistance and a mechanical strength, and corrosion resistance.

[0010]

[Formula 3]



[0011](However, X and Y are a hydrogen atom or a univalent organic group independently, respectively, R^1 is an organic group of with a carbon numbers of two or more m value, and m is an integer of 2-10.)

[0012]

[Formula 4]

$\text{N}^* \text{C-O-Ph-R}^2 \text{-Ph-O-C}^* \text{N} \cdots$ Formula 2 [0013](However, -Ph- is a phenylene group and R^2 expresses a single bond, S, O, CH_2 , SO_2 , or $\text{C}(\text{CH}_3)_2$.)

[0014]In the polymaleimide expressed with the formula 1, if the example of an organic group expressed with -R^1 - is given, -Ph-, -Ph- CH_2 -Ph-, -Ph-O-Ph-, -Ph- SO_2 -Ph-, etc. will be mentioned. However, in this specification, -Ph- shows a phenylene group.

[0015]Although X and Y are a hydrogen atom or a univalent organic group independently, respectively, the smaller one of the molecular weight is preferred at the point that crosslinking reaction advances easily, and it is preferred that X and Y are especially hydrogen atoms. In this invention, X or Y cannot use the polymaleimide which consists of halogen. For example, when X or Y is a chlorine atom, hydrogen chloride may occur and an electrode may be corroded. m is an integer of $2 \leq m \leq 10$.

[0016]The following compounds will be mentioned if the example of polymaleimide expressed with the formula 1 is given. N,N'-ethylene bismaleimide, N,N'-hexamethylene bismaleimide, N,N'-(1,3-phenylene) bismaleimide, N,N'-[1,3-(2-methylphenylene)] bismaleimide, N,N'-(1,4-phenylene) bismaleimide, bis(4-maleimide phenyl)methane, Bis(3-methyl-4-maleimide phenyl)methane, bis(4-maleimide phenyl)ether, A bis(4-maleimide phenyl)sulfone, a bis(4-maleimide phenyl)sulfide, bis(4-maleimide phenyl)ketone, bis(4-maleimide cyclohexyl)methane.

[0017]1,4-bis(4-maleimide phenyl)cyclohexane, 1,4-bis(maleimide methyl)cyclohexane, 1,4-bis(maleimide methyl)benzene, 1,3-bis(4-maleimide phenoxy)benzene, 1,3-bis(3-maleimide phenoxy)benzene.

[0018]Bis[4-(3-maleimide phenoxy) phenyl] methane, bis[4-(4-maleimide phenoxy) phenyl] methane, 1,1-bis[4-(3-maleimide phenoxy) phenyl] ethane, 1,1-bis[4-(4-maleimide phenoxy) phenyl] ethane, 1,2-bis[4-(3-maleimide phenoxy) phenyl] ethane,

1,2-bis[4-(4-maleimide phenoxy) phenyl] ethane, 2,2-bis[4-(3-maleimide phenoxy) phenyl] propane, 2,2-bis[4-(4-maleimide phenoxy) phenyl] propane, 2,2-bis[4-(3-maleimide phenoxy) phenyl] butane, 2,2-bis[4-(4-maleimide phenoxy) phenyl] butane, 2,2-screw [4-(3-maleimide phenoxy) phenyl]-1,1,1,3,3,3-hexafluoropropane, 2,2-screw [4-(4-maleimide phenoxy) phenyl]-1,1,1,3,3,3-hexafluoropropane.

[0019]4,4'-bis(3-maleimide phenoxy)biphenyl, 4,4'-bis(4-maleimide phenoxy)biphenyl, Bis[4-(3-maleimide phenoxy) phenyl] ketone, bis[4-(4-maleimide phenoxy) phenyl] ketone, A bis[4-(3-maleimide phenoxy) phenyl] sulfide, a bis[4-(4-maleimide phenoxy) phenyl] sulfide, A bis[4-(3-maleimide phenoxy) phenyl] sulfoxide, a bis[4-(4-maleimide phenoxy) phenyl] sulfoxide, a bis[4-(3-maleimide phenoxy) phenyl] sulfone, a bis[4-(4-maleimide phenoxy) phenyl] sulfone.

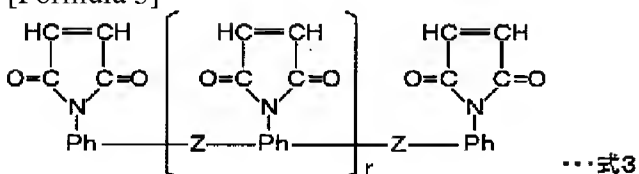
[0020]Bis[4-(3-maleimide phenoxy) phenyl] ether, bis[4-(4-maleimide phenoxy) phenyl] ether, 1,4-bis[4-(4-maleimide phenoxy)-alpha and alpha-dimethylbenzyl] benzene, 1,3-bis[4-(4-maleimide phenoxy)-alpha and alpha-dimethylbenzyl] benzene, 1,4-bis[4-(3-maleimide phenoxy)-alpha and alpha-dimethylbenzyl] benzene, 1,3-bis[4-(3-maleimide phenoxy)-alpha and alpha-dimethylbenzyl] benzene, 1,4-bis[4-(4-maleimide phenoxy)-3,5-dimethyl- alpha and alpha-dimethylbenzyl] benzene, 1,3-bis[4-(4-maleimide phenoxy)-3,5-dimethyl- alpha and alpha-dimethylbenzyl] benzene, 1,4-bis[4-(3-maleimide phenoxy)-3,5-dimethyl- alpha and alpha-dimethylbenzyl] benzene, a 1,3-screw [4-(3-maleimide phenoxy)-3,5-dimethyl- alpha and alpha-dimethylbenzyl].

[0021]A compound expressed with the formula 3 can also be used. This polymaleimide compound is a polymaleimide compound produced by making carry out condensation and dehydration under an acid catalyst in polyamine and a maleic anhydride which are resultants with aniline, formaldehyde or alpha, and alpha'-dichloro-p-xylene.

Polymaleimide illustrated above may be independent, or two or more sorts may be mixed and used for it.

[0022]

[Formula 5]



[0023](However Z being a methylene group or p-xylylene group $0 < r \leq 8$.)

[0024]The diamine made to react to the polymaleimide expressed with the formula 1 in this invention will not be limited especially if it is polymaleimide and diamine in which a reaction is possible. The following compound will be mentioned if a concrete example is given.

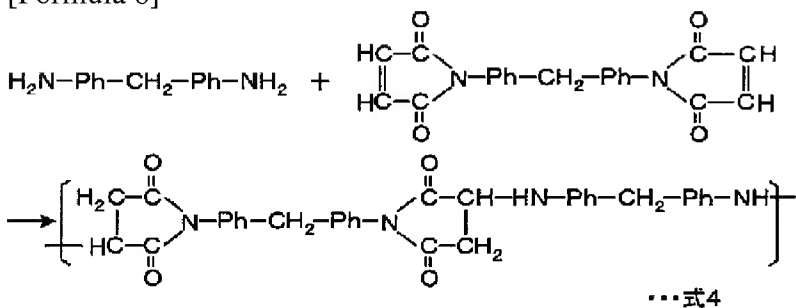
[0025]Diethylenetriamine, triethylenetetramine, tetraethylenepentamine, Hexamethylenediamine, N-aminoethyl piperazine, a 1,4-bis(aminopropyl)piperazine, Trimethyl hexamethylenediamine, a meta-phenylenediamine, a p phenylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylpropane, 4,4'-diaminodiphenylethane, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone, Para -**** (4-aminophenoxy) benzene, Metha- bis(4-aminophenoxy)benzene, 4,4'-diaminodiphenyl ether, A 4,4'-diamino diphenyl sulfide, 1,5-diaminonaphthalene, a 3,4'-diaminobenzanilide, 3,4'-diaminodiphenyl ether, 3,3'-dimethoxybenzidine, meta-xylylene

diamine, PARAKI silylenediamine. These diamine may be independent, or two or more sorts may be mixed and it may be used.

[0026]In this invention, a compound obtained by the reaction of the following [reactant / of polymaleimide and diamine which are expressed with the formula 1] for example, is mentioned.

[0027]

[Formula 6]



[0028]Although JISHIANETO made to react to the polymaleimide expressed with the formula 1 in this invention is expressed with the formula 2, the following compound is mentioned as the example.

[0029]

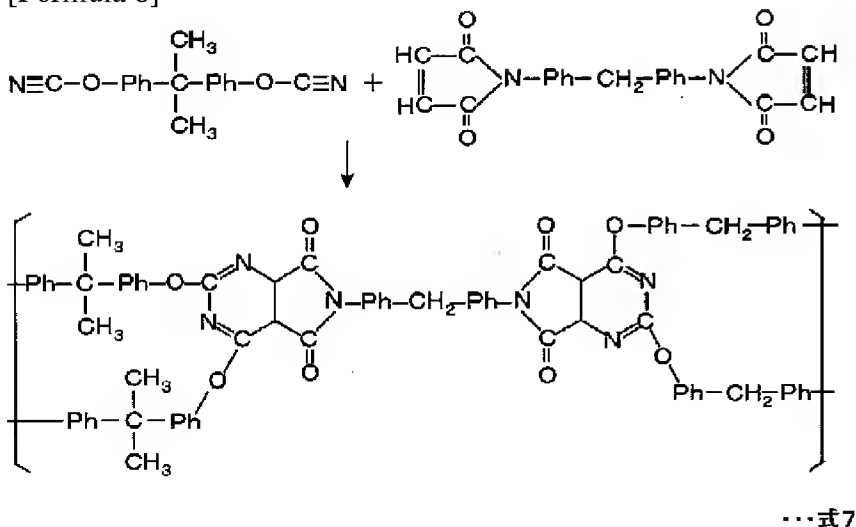
[Formula 7]

N**C-O-Ph-C(CH₃)₂-Ph-O-C**N ... Formula 5 N**C-O-Ph-CH₂-Ph-O-C**N ...

Formula 6[0030]The compound obtained, for example by the following reaction as a reactant with the JISHIANETO compound expressed with the polymaleimide expressed with the formula 1 in this invention and the formula 2 is mentioned.

[0031]

[Formula 8]



[0032]The electroconductive glue for joining the electrode and charge collector in this invention is suspension which contains an above-mentioned addition condensation type imido group content compound as a binder component, and conductive powder is contained in order to give conductivity. Although there is a thing of a metal system and a

nonmetallic system as conductive powder, since the powder of a metal system may make a local cell, it is preferred to use nonmetal system conductive powder. Since electric corrosion resistance is needed for conductive powder, especially use of carbon system materials, such as carbon black and black lead, is preferred.

[0033]In order to improve wettability with resin used as a binder, and dispersibility, conductive powder may mix finishing agents, such as about 1% of the weight of fatty acid, and various silane coupling agents, to this powder, and may perform a surface treatment. In addition, additive agents, such as a leveling agent and a dispersing agent, may be added.

[0034]As for the rate of the addition condensation type imido group content compound contained in a conductive glue line, in this invention, it is preferred that it is 10 to 70 % of the weight to the total amount of conductive powder and an addition condensation type imido group content compound. At less than 10 % of the weight, since the intensity of a glue line falls, and conductivity will fall rapidly if a good adhesive property is not acquired but it exceeds 70 % of the weight, it is not desirable. 20 to 60 % of the weight is especially preferred.

[0035]In an electric double layer capacitor of this invention, since the heat resistance of a hardened material of an addition condensation type imido group content compound which is a binder component of a conductive glue line is high, also after joining a charge collector to an electrode, the dry removal of the moisture in activated carbon can be highly carried out by heating under an elevated temperature, or heat-treatment under decompression. The above-mentioned hardened material has the tolerance over organic electrolysis liquid, and adhesive strength to charge collectors, such as metal etc. of an electrode sheet which uses fluorine-containing resin as a binder, is also extremely excellent. For this reason, even if it repeats a charging and discharging cycle with large current density and impresses voltage over a long period of time, the operation performance is stable, and an increase in internal resistance of an electrode can also be made small.

[0036]In order to join an electrode to a charge collector using electroconductive glue, an addition condensation type imido group content compound comes to hand as powder or a varnish, dissolves in a solvent, and uses as adhesives suspension which made this distribute carbon black and graphite particles highly as a conductive filler. Coating of these adhesives is carried out on the surface of a charge collector, they carry and stick by pressure an electrode sheet subsequently to this surface produced separately, and can join an electrode to a charge collector firmly by carrying out stoving under decompression further under a not less than 200 °C elevated temperature preferably.

[0037]As the above-mentioned solvent, an addition condensation type imido group content compound can be dissolved, especially if it evaporates at a process which carries out stoving, it will not be limited, but various solvents can be used. Specifically N-methyl-2-pyrrolidone, dimethylformamide, Acetone, methyl ethyl ketone, a tetrahydrofuran, xylene, chloroform, toluene, dimethyl sulfoxide, cyclohexane, acetonitrile, dioxane, wood ether, etc. may be mentioned, these solvents may be independent, or two or more sorts may be mixed and they may be used.

[0038]Since intensity can also do capacity highly greatly as specific surface areas are 700-2500m²/g, especially 1000-2000m²/g, a carbon material of an electrode of an electric double layer capacitor of this invention is preferred. Although activated carbon, carbon

black, poly acene, etc. are mentioned as a carbon material, it is preferred to use especially activated carbon powder, and it is still more desirable when high conductivity carbon black is used adding as a conducting material. In this case, as for a conducting material, it is preferred to be contained five to 20% of the weight in an electrode.

[0039] Although an anode and a negative electrode constitute an electric double layer capacitor using the above-mentioned electrode, either an anode or a negative electrode may be used as the above-mentioned electrode, and a chargeable and dischargeable nonpolarizable electrode material, i.e., active material material for rechargeable batteries, may usually be used for another electrode as the main ingredients.

[0040] It is preferred that fluorine-containing resin is contained in an electrode in this invention as a binder. Since a small quantity also gives intensity to an electrode and cannot check the conductivity of an electrode easily by having heat resistance and chemical resistance and making them fibrose, especially polytetrafluoroethylene is preferred. As for intensity of an electrode, and a viewpoint of conductive balance to a binder, it is preferred to be contained five to 20% of the weight in an electrode.

[0041] The charge collector which electrically connects the above-mentioned electrode should just be a material which is excellent in conductivity and is electrochemically durable. Carbon system materials, such as conductive rubber containing the precious metals, such as valve metals, such as aluminum, titanium, and tantalum, stainless steel, gold, and platinum, black lead, glassy carbon, and carbon black, etc. can use it preferably. Since it was lightweight, and it excelled in conductivity and is electrochemically stable especially, aluminum is preferred.

[0042] As for an electrode, it is preferred to be joined to a charge collector via electroconductive glue, after fabricating to a sheet shaped, and as a manufacturing method of an electrode, after it kneads a mixture of activated carbon powder, carbon black, fluorine-containing resin, and fluid lubrication material, for example, it is rolled, and it is fabricated to a sheet shaped. Beforehand, an obtained sheet like electrode carries electroconductive glue on a field which carried out coating, sticks it to a charge collector by pressure, and preferably, under a not less than 200 °C elevated temperature, by carrying out stoving under decompression still more preferably, electroconductive glue hardens it and it can join an electrode to a charge collector firmly. For a productivity drive of an electrode body, it is still more preferred to carry out reduced pressure drying at 250-400 °C.

[0043] An electrode makes a solution which dissolved fluorine-containing resin in a solvent distribute a carbon material, may carry out coating of a slurry, and nothing and this slurry to a charge collector, and may form them. It is preferred to carry out coating of the slurry on a field which carried out coating of the electroconductive glue to a charge collector beforehand, and to carry out stoving under a not less than 200 °C elevated temperature, especially decompression also in this case.

[0044] Organic electrolysis liquid in particular used for an electric double layer capacitor of this invention is not limited, but can use organic electrolysis liquid which contains salts of ionic dissociation nature in a publicly known organic solvent. inside -- $R^1R^2R^3R^4N^+$ and $R^1R^2R^3R^4P^+$ (R^1 .) To R^2 , R^3 , R^4 , and ***** independence, the 4th class onium cations, such as an alkyl group of the carbon numbers 1-6, It is preferred to use organic electrolysis liquid made to dissolve a salt which consists of anions, such as BF_4^- , PF_6^- , ClO_4^- , and $CF_3SO_3^-$, in an organic solvent.

[0045]As the above-mentioned organic solvent, lactone, such as carbonate, such as propylene carbonate, butylene carbonate, and diethyl carbonate, and gamma-butyrolactone, sulfolane, or these mixed solvents can use it preferably.

[0046]It is preferred to use a ***** electrolysis solution.

EXAMPLE

[Example]Hereafter, although an example (Examples 1-5) and a comparative example (Example 6) explain this invention further, this invention is not limited to these.

[0048]The coconut obtained by the steam activation method 80 % of the weight of ***** (mean-particle-diameter [of 10 micrometers], and specific surface area $1800\text{m}^2/\text{g}$), Ethanol was added and kneaded into the mixture which consists of 10 % of the weight of PTFE, and 10 % of the weight of carbon black, kneaded material was fabricated to the sheet shaped, and it acted as roll pressure Nobu to 0.3 mm in thickness further. The electrode sheet of 40 mm squares was cut out from this sheet, coating of the electroconductive glue shown in the surface of the charge collector which consists of aluminium foil (0.1 mm in thickness) which performed the etching process below was carried out, and it was stuck to this surface by pressure, it heated under decompression for 3 hours, and the drying process was carried out. Move to the glove box filled with argon gas after desiccation, and an electrode is enough impregnated with the propylene carbonate solution which contains 1 mol/l. of tetraethylammonium tetrafluoroborate as organic electrolysis liquid, Inter-electrode [of two sheets] was made to counter on both sides of the separator paper which consists of a nonwoven fabric of a polypropylene fiber, and the electric double layer capacitor was assembled.

[0049]After measuring the early service capacity and internal resistance of an electric double layer capacitor which were obtained, the service capacity and internal resistance after a 3000 cycle repetition and 3000 cycles were measured for the charge and discharge by the constant current of 1A between 0-2.8V in a 40 ** thermostat. By comparing the performance change before and behind a charging and discharging cycle, the long-term working reliability of the electric double layer capacitor was evaluated accelerative. A result is shown in Table 1.

[0050][Electroconductive glue (1)] Bismaleimide and bisphenol A JISHIANETO made the acetone solution 25g which contains bismaleimide triazine resin (Mitsubishi Gas Chemical Co., Inc. make and trade name:BT2170) which is the main ingredients 20% of the weight distribute the graphite particles 5g, and made this electroconductive glue (1).

[0051][electroconductive glue (2)] -- instead of [of BT2170] -- bis(4-maleimide phenyl)methane (the Mitsui Toatsu Chemicals, Inc. make.) Trade name:

Electroconductive glue (2) as well as electroconductive glue (1) was prepared except having used [BMI-S] dimethylformamide for 4.5 g and 4,4'-diaminodiphenylmethane (the Mitsui Toatsu Chemicals, Inc. make, trade name:MDA-220) instead of 0.5 g and acetone.

[0052][Electroconductive glue (3)] Electroconductive glue (3) as well as electroconductive glue (1) was prepared except having used conductive-carbon-black powder instead of graphite particles.

[0053][Electroconductive glue (4)] Methyl ethyl ketone was used instead of acetone, and electroconductive glue (4) as well as electroconductive glue (1) was prepared except

having made concentration of BT2170 into 40 % of the weight.

[0054][electroconductive glue (5)] -- the polyamino bismaleimide resin (made in Rolle Poulain.) a maleic anhydride and whose 4,4'-diaminodiphenylmethane are the main ingredients instead of BT2170 Trade name: Electroconductive glue (5) as well as electroconductive glue (3) was prepared except having used KERUIMIDO 601.

[0055][Electroconductive glue (6)] Electroconductive glue (6) as well as electroconductive glue (1) was prepared except having used polyvinyl alcohol (Japanese synthetic-chemistry company make, a trade name: Gosenol) instead of BT2170.

[0056]Temperature which carries out reduced pressure drying in order to join an electrode sheet and a charge collector was carried out as in Table 1 in consideration of the heat-resistant temperature of the binder of the adhesives to be used.

[0057]

[Table 1]

	導電性 接着剤	減圧乾燥 の温度	初期物性		サイクル試験後	
			容量／F	抵抗／Ω	容量／F	抵抗／Ω
例 1	(1)	3 0 0℃	1 5 . 4	0 . 5 0	1 4 . 6	0 . 5 0
例 2	(2)	3 0 0℃	1 5 . 3	0 . 5 1	1 4 . 6	0 . 5 0
例 3	(3)	3 0 0℃	1 5 . 5	0 . 5 1	1 4 . 7	0 . 5 0
例 4	(4)	3 0 0℃	1 5 . 0	0 . 5 3	1 4 . 5	0 . 5 1
例 5	(5)	3 0 0℃	1 5 . 2	0 . 5 2	1 5 . 6	0 . 5 1
例 6	(6)	1 2 0℃	1 4 . 4	0 . 6 6	8 . 4	1 . 3 0

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- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.